

SOLUBILITY OF NITROGEN  
IN FUSED SODIUM NITRATE

by

LAWRENCE SEIBLES

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## LIST OF SYMBOLS

$\underline{C}_d$	concentration of dissolved gas
$\underline{C}_g$	concentration of gas in the gas phase
$\underline{E}$	energy
$\Delta \underline{G}$	free energy change
$\Delta \underline{H}$	heat of solution
$\underline{K}_c$	distribution coefficient
$\underline{K}_p$	Henry's law constant
$\underline{P}$	pressure
$\underline{R}$	gas constant
$\Delta \underline{S}_p$	entropy of solution
$\underline{T}$	absolute temperature
$\underline{V}$	molar volume of gas
$\underline{d}_{t,1}$	density of salt at $t^\circ\text{C}$ and 1 atm.
$\underline{d}_{t,p}$	density of salt at $t^\circ\text{C}$ and p atm.
$\underline{k}$	Boltzmann constant
$\underline{k}'$	correction factor of eq. 10.
$\underline{m}$	mass
$\underline{r}$	radius of gas molecule
$\underline{t}$	centigrade temperature
$\underline{\gamma}$	surface tension of salt

## INTRODUCTION AND THEORY

### I. Purpose of the Investigation

The solubilities of gases in liquids, including the solubilities of noble gases in various organic solvents, have been studied by many investigators (1-7). However, investigations of the solubility of gases in molten salt systems have been studied only recently. These investigations were begun as a consequence of the production of xenon and krypton as by-products in high-temperature nuclear reactors. The presence of these gases in the reactor could possibly lead to undesirable perturbations in nuclear reactivity. It was, therefore, desirable to know the solubilities and their temperature dependences for such gases in the molten fluoride mixtures used in the operation of these reactors.

Fused salt systems offer a radically different solvent medium for the study of gas solubilities. Recent studies of the solubilities of noble gases in molten fluoride eutectic mixtures (8-10) indicate that the solubility of a gas in molten salts depends to a large extent on the size and polarizability of the gas molecule, and on the surface tension of the melt.

The purpose of this work is to present new data for gas solubilities in molten salts. The work includes: (a) solubility measurements of nitrogen in molten sodium nitrate from 623°K to 727°K and at pressures ranging from 140 atm. to 426 atm., (b) the calculations of the heat and entropy of solution, and (c) an explanation of the results in terms of the size and polarizability of the gas molecule, and the surface tension of the melt.

### II. Theoretical Considerations

The solubility of a gas in a liquid depends on the nature of the gas and the liquid, and on the pressure and temperature. The solubility is

relatively small in most cases, and is consequently governed by the thermodynamics of dilute solutions (11, 12). One of the general features of these principles is that, at constant temperature, there is a linear relation between the equilibrium pressure of the gas above the solution and the concentration of gas dissolved in the solution. This linear relation between concentration and pressure is known as Henry's law, and is given by

$$\underline{m} = \underline{K}_p \underline{P} \quad 1.$$

where  $\underline{m}$  is the mass of gas dissolved in a unit volume of solvent in equilibrium with the gas phase at pressure  $\underline{P}$  (at constant temperature), and  $\underline{K}_p$  is Henry's law constant which is independent of the pressure. This relation is expected from kinetic considerations, since compression of a gas tends to increase its solubility. Henry's law constant depends on the temperature and the nature of the gas and the solvent, and is the slope of the solute concentration versus pressure curve, as the solute concentration approaches zero.

Henry's law can also be expressed in another familiar form. Since the mass of gas dissolved per unit volume,  $\underline{m}$ , is the concentration in g. cm.<sup>-3</sup> then it is proportional to the concentration expressed in moles of solute per liter of solution, since the volume change on solution is considered to be negligibly small. Also, the pressure,  $\underline{P}$ , of the gas in equilibrium with the solution is proportional to the number of molecules in the gas phase in terms of moles per liter. Therefore, if  $\underline{C}_d$  represents the concentration of the dissolved gas in moles per liter of solvent, and  $\underline{C}_g$  represents the concentration of the gas phase in moles per liter, then Henry's law is given by

$$\underline{K}_c = \underline{C}_d / \underline{C}_g \quad 2.$$

where  $K_c$  is usually known as the distribution ratio or Ostwald's coefficient of solubility (13). The significance of this distribution coefficient will be discussed in later sections.

The molecular basis of Henry's law can be understood from the fact that in dilute solutions the solute molecules will be isolated from one another and surrounded by solvent molecules. Henry's law applies as long as the solute molecules never approach one another closely enough to interact significantly, because the escaping tendency is then proportional to the number of solute molecules in the fixed amount of solvent. The intermolecular interaction potential between non-polar molecules, or between rotating dipolar molecules, decreases as  $r^{-6}$ , where  $r$  is the intermolecular distance. Thus, the interaction energy decreases very rapidly with increased separation. There are two principal exceptions to these conclusions: (a) if the solute molecules are very large, such as high polymer molecules, then the probability that the solute molecules are close together is much greater, and (b) if the solute molecules possess electrical charges, the intermolecular potential decreases only as  $r^{-1}$  or less (12).

The temperature dependence of Henry's law constant is expressed by the Van't Hoff equation (12)

$$d(\ln K_p)/dT = \Delta H_{\text{soln.}}/RT^2 \quad 3.$$

where  $\Delta H_{\text{soln.}}$  is the heat of solution. Integration of this equation yields

$$\log K_p = -\Delta H_{\text{soln.}}/2.303 RT + \text{constant} \quad 4.$$

Therefore, a plot of  $\log K_p$  versus  $1/T$  should yield a straight line whose slope is given by  $-\Delta H_{\text{soln.}}/2.303 R$ , from which the heat of solution can be obtained. If the solubility increases with temperature, this slope will be negative, and the heat of solution will be positive. The reverse is true when the solubility decreases with temperature.

The interpretation of gas solubility by Uhlig (13) expresses the solubility as a function of the molecular radius of the gas and the surface tension of the solvent. The gas molecule is assumed to be spherical, and the surface tension of the solvent is assumed to be the same for molecular dimensions as it is for the macroscopic bulk. It is proposed that when a gas molecule of radius  $r$  enters the solvent, it produces a spherical cavity of essentially the same radius. A certain amount of work is done in producing this cavity, since any increase in surface area of the liquid is associated with a definite energy change. This energy,  $E_1$ , is given by the increase in area, due to creation of the cavity, multiplied by the surface tension of the solvent,  $\gamma$ ,

$$E_1 = 4\pi r^2 \gamma \quad 5.$$

where  $r$  is the gas molecule's radius in Angstroms, and  $\gamma$  is the surface tension of the solvent in dynes cm.<sup>-1</sup>. In addition to this latter term, there are energy terms arising from solute-solvent interactions, which account for repulsive and attractive forces at the intermolecular distances characteristic of molecular separations in liquids. The nature and magnitude of these forces depend on the specific properties of the solute and solvent molecules, which, in general, present a complex picture too difficult to resolve using present-day theories of molecular interactions. However, a qualitative picture is possible, since, for example, interactions would be expected to be large and positive between gas and solvent molecules containing polar groups, with or without a resultant moment, and relatively small and negative for an elementary gas dissolved in a non-polar solvent. All the energies in this category are termed "interaction energies" and are designated as  $E_2$ . Then the energy change,  $\Delta E$ , of the system, in transferring a molecule from the solvent phase to the gas phase,

is given by

$$\Delta \underline{E} = 4\pi r^2 \gamma - \underline{E}_2 \quad 6.$$

where the interactions between the gas phase solute molecules and the gas phase solvent molecules are neglected, since these are small except at high solvent vapor pressures. The Maxwell-Boltzmann distribution theorem gives the distribution ratio of the solute molecules between the two phases as

$$\underline{K}_c = \underline{C}_d / \underline{C}_g = \exp (-\Delta \underline{E} / kT) \quad 7.$$

where  $\underline{C}_d$  and  $\underline{C}_g$  are the concentrations of the solution and gas phase respectively, and  $k$  is the Boltzmann constant. The following relation is obtained by combining eq. 6. and 7.

$$\ln \underline{K}_c = -4\pi r^2 \gamma / kT + \underline{E}_2 / kT \quad 8..$$

From the above equation, one would expect that if the interaction energy remained constant, the solubility would increase with decreasing gas molecular radius and decreasing surface tension of the solvent. Also, for gases in which the solute-solvent interactions are expected to be small (for example with the noble gases), for a variety of solvents, the solubility would depend primarily on the first term of the equation. For this type of system the plot of  $\ln \underline{K}_c$  versus the surface tension of the solvent should be linear and have a slope proportional to the square of the molecular radius of the gas. The intercept of the plot would be a measure of the interaction energy.

From the solubility data for several gases, including  $O_2$ ,  $N_2$ ,  $H_2$ , and  $CH_4$ , in a variety of solvents, Uhlig found that the interaction energy was approximately constant for any one gas and independent of the nature of the solvent (13). Also, if  $4\pi r^2 \gamma > \underline{E}_2$ , the solubility of the gas increased with temperature, and when  $4\pi r^2 \gamma < \underline{E}_2$ , the solubility decreased with temperature. The gas molecular radii were calculated from the experi-

mental plots and were found to be smaller than those calculated from van der Waals constants. This indicated that the estimated sizes of the spherical cavities were perhaps too small, especially when the thermal motions of the gas molecules are considered.

In the simplified model of Blander, Grimes, Smith, and Watson (9), the theoretical distribution ratio,  $K_c$ , for an inert gas in solution equilibrium with a fused salt, is derived by equating the free energy of solution of the gas to the free energy of formation of holes the size of the gas molecules in a continuous fluid having the same surface tension as the solvent. Although the model is naive it yields an interesting correlation with experiment. If a molecule does not interact with the liquid in which it is dissolved, the solubility of the gas can be estimated from the free energy changes for the following steps:

- (a) The gas is expanded from the concentration  $C_g$  in the gas phase to the concentration  $C_d$  of the solution. The free energy change for this step is given by

$$\Delta G_1 = RT \ln (C_d/C_g) \quad 9.$$

- (b) The gas atoms are contracted to "point particles" and are poured into the liquid. The free energy change for this step is given as  $\Delta G_2$ .

- (c) The "point particles" are then expanded back to their original sizes. The free energy change for this step is given by

$$\Delta G_3 = k'A \gamma_{mic} - \Delta G_2 \quad 10.$$

where  $A$  is the area of the hole created by the particle when it is expanded back to its original size,  $\gamma_{mic}$  is the microscopic "surface tension" of the solvent, and  $k'$  is a constant necessary to obtain the correct units of energy. Since the molecules are assumed to be spherical,  $k'A = 18.08 r^2$ ,

where  $\underline{r}$  is the effective molecular radius in Angstroms. The summation of the free energy changes for the over-all process is zero, if the system is in equilibrium, and the derived relation is thus

$$\underline{K}_{c, \text{theor.}} = \underline{C}_d / \underline{C}_g = \exp (-18.08 \underline{r}^2 \underline{\gamma} / \underline{RT}) \quad 11.$$

where  $\underline{\gamma}_{\text{mic}}$  is generally taken as the macroscopic value,  $\underline{R}$  is the gas constant, and  $\underline{T}$  is the absolute temperature. This model neglects solvation effects in comparison to the large endothermic work done against the high surface tension of a typical ionic liquid to accommodate a gas molecule. This approach is justified reasonably well by the cited authors' (9) observations of endothermic heats of solution for various noble gases in molten fluoride mixtures. As the solvation effects, such as ion-induced dipole, become more pronounced, the associated exoenergetics would be expected to contribute to the over-all heat of solution to an ever-increasing extent. At some point, therefore, the solvation energy associated with a given solute may exceed the endoenergetics of molecular cavity creation, resulting in the more usually observed exothermic heat of solution. This effect would be even more enhanced if solvents of lower surface tension were employed. Increasing solvation effects naturally bring about a greater gas solubility at a given temperature and pressure, which in turn causes an increasing trend in the ratio  $\underline{K}_{c, \text{exp.}} / \underline{K}_{c, \text{theor.}}$ . Such was the case observed in reference (9), as solvation effects increased with increasing polarizability of the noble gas solute atom employed. The magnitude and variation of the solubility with size of the gas molecule were correctly predicted, with the solubility increasing with decreasing size of the noble gas molecule. Also, the endothermic heats of solvation increased with increasing atomic weight of the noble gas. The theoretical aspects of fused salt-gas solvations and their energetics have been amply reviewed and discussed

by Stillinger (14). In the later work of Shaffer, Grimes, and Watson (15), on the solubility of HF in molten fluorides, the solvation effects obviously were dominant over the endothermic work against surface tension, resulting in fairly high solubilities and exothermic heats of solution.

## EXPERIMENTAL

### I. Chemicals

Reagent grade  $\text{NaNO}_3$  was obtained from the Baker and Adamson Company. The samples were heated to over the melting point to remove moisture. Residues, if any, were removed with a porcelain spatula, or the salt was decanted. The sample was cooled in a desiccator, and was then crushed to a powder for weighing into a Pyrex bomb liner.

Nitrogen gas, 99.98% pure, bone dry grade, was obtained from the National Cylinder Gas Company.

### II. Apparatus

#### A. Commercial Equipment

A 500-ml capacity Inconel metal bomb, Type A243HC5 of the Parr Instrument Company, was fitted, according to specifications by J.L. Copeland, with two CONAX No. TG-20-A-2-L thermocouple glands packed with "Lava", a natural magnesium silicate. Maximum safe working pressure of the bomb was from 7,500 p.s.i.g. at  $25^\circ\text{C}$  to 5,100 p.s.i.g. at  $600^\circ\text{C}$ , as specified by the Parr Instrument Company engineers. A Super-Gauge, made by the U.S. Gauge Division of Ametek, was connected to the bomb. This gauge measures pressures to 8,000 p.s.i.g., and is calibrated in divisions of 100 p.s.i.g. The accuracy of this gauge, as quoted by the manufacturer, is  $\pm 40$  p.s.i.g., or slightly less than  $\pm 3$  atm. Both of the CONAX glands contained chromel-alumel thermocouples, one of which measured the salt temperature and was protected by an Inconel metal tube plus an outer tube of Pyrex glass. The other thermocouple was protected by a Pyrex tube, and was used to measure the gas temperature. The manufacturer's precalibrated accuracy of each of the thermocouples was  $\pm 0.5^\circ\text{C}$ . The bomb was sealed by a heavy-duty copper

gasket (seated in grooves in the head and cylinder) with eight cap screws in a hardened steel ring, split in halves. These ring sections are retained by a heavy steel band. A photograph of the entire bomb assembly is given in reference (16).

The vacuum pump used was a Genco HYVAC No. 91105. When a gas pressure greater than that in the gas cylinder was required, an Aminco air-operated, single-ended diaphragm type compressor was used. This vertical unit consists of a six-inch single shaft air operator connected directly to a hydraulic plunger which transmits pressure to a hydraulic medium. This in turn causes a stainless steel diaphragm to flex and to compress gas into the head. The unit is rated for a maximum delivery pressure of 10,000 p.s.i.g. This type of compressor is advantageous in that the gas to be compressed comes in contact only with a metal diaphragm and not with oil or water.

The chromel-alumel thermocouple leads from the bomb were connected to a Rubicon potentiometer No. 2703 with an internal standard cell. A  $-10^{\circ}$  to  $110^{\circ}\text{C}$  thermometer, placed at the potentiometer terminals, was used to record room temperature.

#### B. Constructed Equipment

A Pyrex liner was used as the salt container to protect the bomb from corrosion. The diameter of the liner was 6 cm. o.d., and its length was 15 cm. It was sealed flat on the bottom.

The furnace was constructed by W.C. Zybko (16). It consisted of one-quarter inch thick Transite outer walls and a 4-inch i.d. Norton Company aluminum oxide core which was fixed vertically in the furnace housing. The outside of the core was wound with 18-gauge Chromel-A wire. Norton Company

Alundum No. RA 1055 refractory cement was placed over the outside of the wire-wound core. Super Stic-Tite asbestos cement served as insulation between the core and walls of the furnace. Temperature in the furnace was maintained with a 220-volt Powerstat and a 0-5 amp. a.c. ammeter.

### III. Procedure

The experimental procedure is adopted from that of W.C. Zybko (16). The reagent grade  $\text{NaNO}_3$  was melted in a porcelain casserole to remove moisture and other impurities. The salt was then transferred to a desiccator and allowed to solidify, after which it was crushed to a fine powder with a mortar and pestle.

The Pyrex liner was cleaned with dichromate cleaning solution, and was rinsed with deionized water. The liner was dried in an oven at about  $130^\circ\text{C}$  and was then allowed to cool in a desiccator. It was then charged with 350-450 g. of the dry, powdered salt, weighed to the nearest 0.5 g.

Once the liner was in the bomb, the head was placed in position and the assembly was sealed. Removal of air and any additional water vapor was assured by pumping out the bomb for about ten minutes. The bomb was charged with  $\text{N}_2$ , at room temperature, to some desired pressure. The compressor was used if this pressure was greater than that in the gas cylinder. The bomb was allowed to stand at room temperature for about one hour to come to a temperature-pressure equilibrium. After equilibrium measurements of pressure and temperature were obtained, the bomb assembly was heated to an initial fused salt temperature of  $454^\circ\text{C}$  (except in one run when the corresponding pressure involved would have exceeded the prescribed safety limits of the bomb), and the equilibrium gas pressure and temperature were noted. The temperature was then lowered to a salt temperature of  $445^\circ\text{C}$ ,

with the system being agitated frequently to ensure equilibrium and to avoid supersaturation of the melt, and the new equilibrium gas pressure and temperature were observed. This stepwise procedure was continued for salt temperatures of 423°C, 413.5°C, 396.5°C, 382.5°C, 368.5°C, and 355.5°C. This experiment was repeated five times for the same eight temperatures, each time with a different starting pressure of  $N_2$  at room temperature. These runs yielded eight solubility isotherms, each consisting of four or five solubility-pressure points. The maximum pressure for any experiment was 426 atm., and the minimum pressure for any run was 140 atm. Molar volumes of  $N_2$  at the various gas temperatures and pressures were obtained from graphs of the  $P$ - $\bar{V}$ - $T$  data compilation of Din (17).

As in previous work (18, 19), the decrease in moles of the gas phase in the system, between a given high temperature and room temperature, was attributed to gas solubility in the melt. The density of liquid  $NaNO_3$  at a given temperature and pressure,  $\underline{d}_{t,p}$ , used for calculating the pure salt's total volume, was obtained from the following empirical equation for the density in the absence of a gas phase

$$\underline{d}_{t,p} = \underline{d}_{t,1} + (3.9 \times 10^{-5}) \underline{P} \text{ g. cm.}^{-3} \quad 12.$$

where  $\underline{d}_{t,1}$  is the density at  $t^\circ C$  and 1 atm., and  $\underline{P}$  is the piston pressure in atm. This relationship is based on the piston pressure-density data of Owens (20). The density  $\underline{d}_{t,1}$  is obtainable from the empirical relation of Bloom, Knaggs, Molloy, and Welch (21)

$$\underline{d}_{t,1} = 2.134 - (7.03 \times 10^{-4}) \underline{t} \text{ g. cm.}^{-3} \quad 13.$$

A minor error persists as a result of using pure salt densities as estimates of the actual dilute solution densities. It is thought that this error is within the experimental error of the procedure. The maximum error in a pressure measurement is slightly less than  $\pm 3$  atm., as quoted by the

gauge manufacturer (18).

Average Henry's law constants,  $\underline{K}_p$ , where

$$\underline{K}_p = \underline{C}_d / \underline{P} \quad \text{moles of gas cm.}^{-3} \text{ atm.}^{-1} \quad 14.$$

( $\underline{P}$  is the gas-saturation pressure in atm.), and distribution coefficients,

$\underline{K}_c$ , were calculated for each solubility-pressure isotherm.

## RESULTS AND CALCULATIONS

The determinations of the solubilities of  $N_2$  in fused  $NaNO_3$  at the various temperatures and pressures were based on the difference between the number of moles of gas in the gas phase at room temperature, with the salt in the solid state, and the number of moles of gas in the gas phase at the higher temperature, in equilibrium with the molten salt. This difference in the number of moles of gas present was calculated using compressibility data for  $N_2$ , which was obtained from detailed plots of the  $P$ - $V$ - $T$  data compiled by Din (17). The volume of gas in the bomb was calculated by subtracting the volume of the salt from the effective volume of the bomb with the empty liner. The solid salt volume was calculated using a density of  $2.261 \text{ g. cm.}^{-3}$  (23). The molten salt volumes at the various temperatures and pressures were calculated using densities obtained from eq. 12 and 13. Thermal expansions of the bomb, Pyrex liner, and thermocouples were ignored since their contributions to the total bomb volume are quite small.

Table I summarizes the experimental pressures, solubilities, Henry's law constants, and distribution coefficients. In addition, theoretical values of the distribution coefficients, calculated from eq. 11, are also included. Surface tension values used in eq. 11 were calculated from the empirical equation of Addison and Coldrey (22) as applied to fused  $NaNO_3$

$$\gamma = 116.6 - 0.050(t - 308) \text{ dynes cm.}^{-1} \quad 15.$$

where  $t$  is the temperature in  $^{\circ}\text{C}$ . An approximate close packed radius of  $2.00 \text{ \AA}$  was taken for the  $N_2$  molecule, regarded as a sphere (24). It is interesting to note that a sample calculation for the expected value of  $r$  for  $N_2$ , using eq. 11 together with an experimental value of  $K_c$  for, say,  $641.5^{\circ}\text{K}$ , yields a value of  $r = 1.16 \text{ \AA}$ . This naive approach gives a value which appears to be too small, especially when Blander, et. al., (9) were forced to accept

effectively larger radii than usual to obtain complete agreement of theory with experiment. The errors recorded for the average Henry's law constants are the probable errors for a single observation.

Figure 1 is a graph of the eight solubility-pressure isotherms, with temperatures as indicated in  $^{\circ}\text{K}$ . The plots are drawn with slopes equal to the tabulated average  $\underline{K}_p$  values. Individual points are not shown for the sake of avoiding confusion; they are available for graphing from Table I. The asterisked values of  $\underline{K}_p$  in Table I were statistically discarded according to Chauvenet's principle (25). Figure 2 depicts the relationship between the common  $\log \underline{K}_{p,\text{av.}}$  and  $1/\underline{T}$  in  $(^{\circ}\text{K})^{-1}$ . The least squares straight line relationship for this graph is

$$\log \underline{K}_p = (597 \pm 19) (1/\underline{T}) - (6.64 \pm 0.03) \quad 16.$$

where the errors are the least squares probable errors, and units of  $\underline{K}_p$  are those of Table I. The theoretical thermodynamic equation for such a plot is (15)

$$\ln \underline{K}_p' = -(\Delta \underline{H}/\underline{R}) (1/\underline{T}) + \Delta \underline{S}_p/\underline{R} \quad 17.$$

where  $\underline{K}_p'$  is in units of  $\text{mole l.}^{-1} \text{ atm.}^{-1}$ ,  $\Delta \underline{H}$  is the heat of solution, and  $\Delta \underline{S}_p$  is the entropy of solution in terms of equal solute gas pressures inside and outside of the liquid. Use of eq. 16 and 17 yields the experimental values

$$\Delta \underline{H} = -2.73 \pm 0.09 \text{ kcal. mole}^{-1} \text{ and } \Delta \underline{S}_p = -16.6 \pm 0.1 \text{ e.u.,}$$

where the errors are again probable errors.

Calculations of the experimental distribution ratios  $\underline{K}_{c,\text{exp.}}$ , are given as defined by eq. 2. It is assumed that  $\underline{C}_d$  is small enough to render the solution ideal, so that the activity of the dissolved gas may be equated to its concentration. Furthermore, ideal gas behavior is assumed for  $\text{N}_2$  at the high temperatures, in spite of the high pressures involved, so that the fugacity may be equated to the pressure.

Table I: Summary of Solubility-Temperature-Pressure  
Data for Nitrogen in Fused Sodium Nitrate  
(Temperatures are those of the Fused Salt)

Gas Pressure, $\underline{P}$ , atm.	Solubility, $\underline{C_d}$ , mole cm. <sup>-3</sup> , x 10 <sup>4</sup>	$\underline{T = 727^\circ \text{K}}$		Theoretical Distribution Coeff., $\underline{K_c}$ , theor., x 10
		Henry's Law Const., $\underline{K_p}$ , mole cm. <sup>-3</sup> atm <sup>-1</sup> , x 10 <sup>7</sup>	Distribution Coeff., $\underline{K_c}$ , expt., x 10	
364	6.00	16.5	1.11	
286	4.00	14.0	0.908	
227	3.11	13.7	0.869	0.042
167	2.73	16.4	1.01	
		$\underline{A_{V_s} = 15.2 \pm 1.2}$	$\underline{A_{V_s} = 0.976}$	
$\underline{T = 718^\circ \text{K}}$				
357	5.97	16.7	1.11	
281	4.21	15.0	0.961	
223	3.37	15.1	0.949	0.039
163	2.98	18.3*	--	
		$\underline{A_{V_s} = 15.6 \pm 0.8}$	$\underline{A_{V_s} = 1.01}$	

		<u>T = 696°K</u>			
349	5.57	16.0	1.04		
272	4.34	16.0	1.00		
217	3.24	14.9	0.915		0.031
159	2.85	17.9	1.07		
		<u>Av. = 16.2 ± 1.0</u>		<u>Av. = 1.01</u>	
		<u>T = 686.5°K</u>			
426	7.40	17.4	1.16		
341	5.93	17.4	1.11		
266	4.66	17.5	1.08		0.027
213	3.31	15.5	0.938		
155	2.91	18.8	1.10		
		<u>Av. = 17.3 ± 0.9</u>		<u>Av. = 1.08</u>	
		<u>T = 669.5°K</u>			
415	6.64	16.0	1.03		
332	5.87	17.7	1.10		
258	4.64	18.0	1.08		0.022
205	3.75	18.3	1.08		
151	3.08	20.4	1.17		
		<u>Av. = 18.1 ± 1.2</u>		<u>Av. = 1.09</u>	



Figure 1. Solubility-Pressure Isotherms for Nitrogen in Fused Sodium Nitrate. (Temperatures are those of the Fused Salt in  $^{\circ}\text{K}$ ).

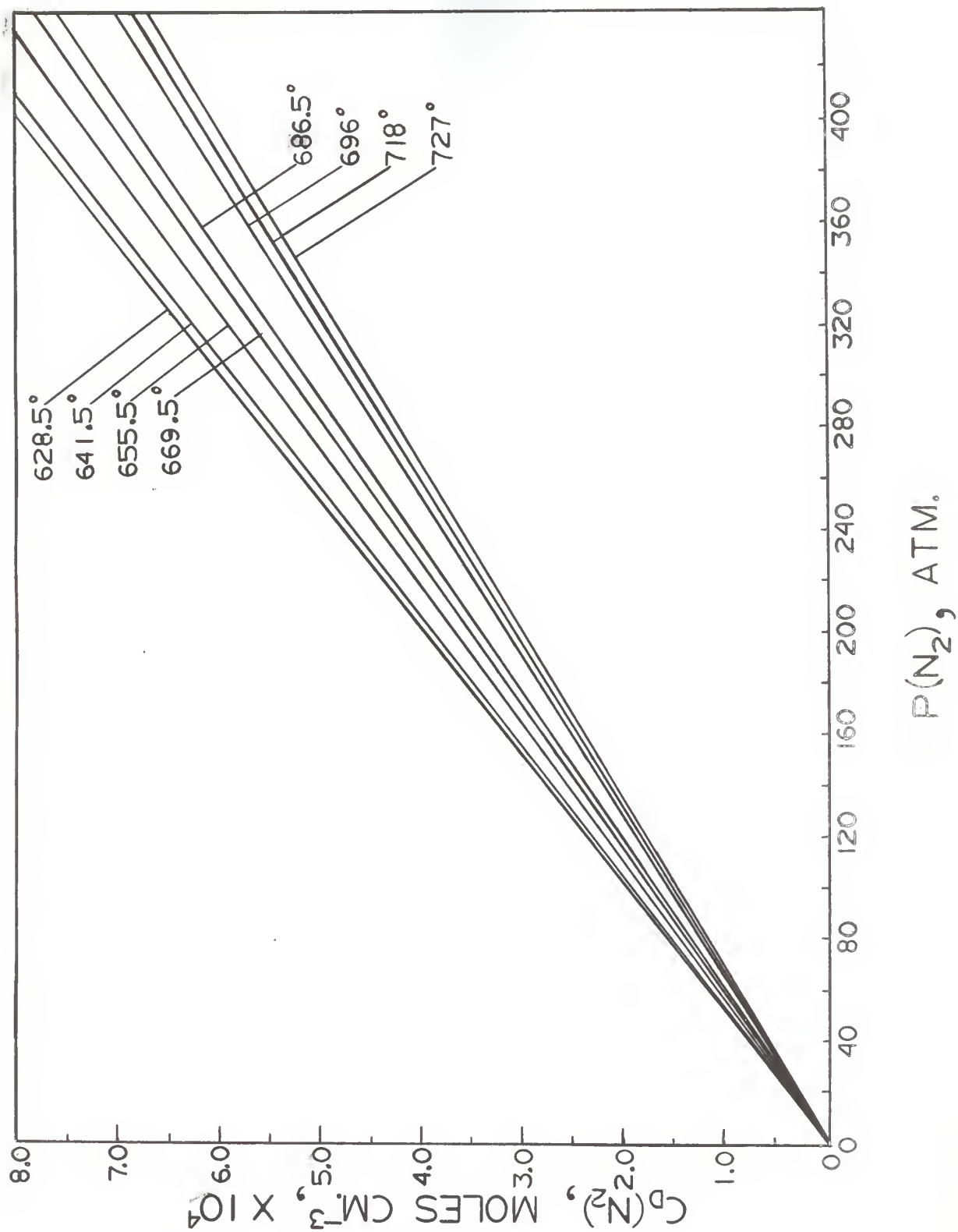
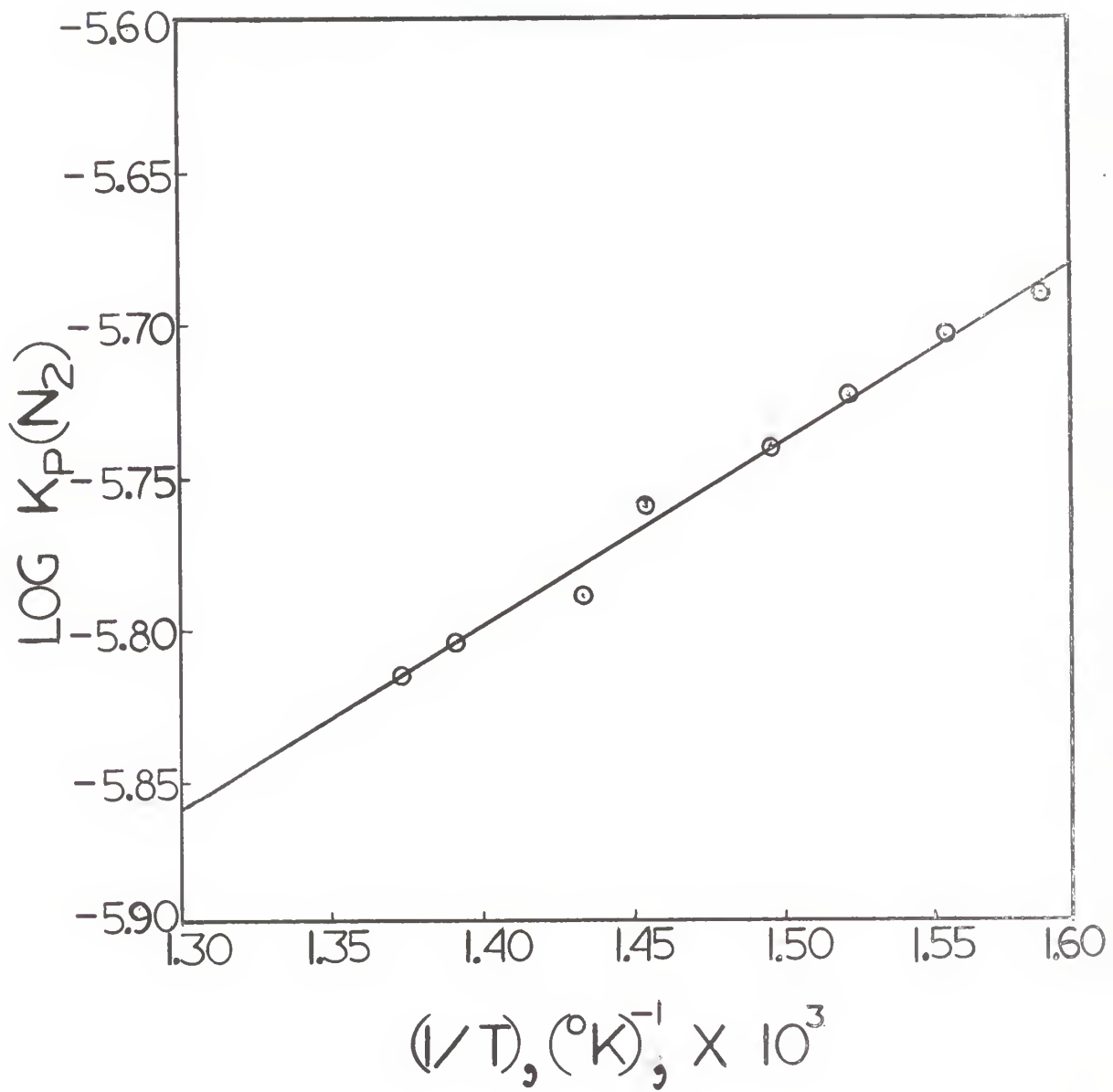


Figure 2. Temperature Dependence of Henry's Law Constant for Nitrogen  
in Fused Sodium Nitrate.



## DISCUSSION

The negative temperature coefficient of solubility for  $N_2$  in fused  $NaNO_3$ , and the attendant exothermic heat of solution, lead to the conclusion that solvation effects in this system are of greater importance than the work required to create a solute molecule cavity. This conclusion is also supported by the large  $K_{c, \text{expt}}/K_{c, \text{theor}}$  ratios,  $K_{c, \text{expt}}$  (average) being from 23 to 83 times greater than  $K_{c, \text{theor}}$ . This ratio is also seen to decrease with temperature. However, no immediate significance can be attached to this trend. Prior work on solubilities of the noble gases in molten fluorides has usually resulted in this ratio being less than unity, with the smallest values for the less polarizable gases such as He and Ne (9, 10). In some of these cases, with more polarizable gases such as Ar and Xe, the ratio was sometimes slightly greater than unity, presumably owing to the effect of greater ion-induced dipole interactions in augmenting the solubility.

Results from the work on solubility of HF in molten fluorides gave experimental heats of solution ranging from  $-3.85 \text{ kcal. mole}^{-1}$ , for 45 mole % of NaF in a NaF- $ZrF_4$  mixture, to  $-9.70 \text{ kcal. mole}^{-1}$  for 80.5 mole % NaF (15). The observed  $\Delta H$  of  $-2.73 \text{ kcal. mole}^{-1}$  for  $N_2$  in  $NaNO_3$  is somewhat smaller than the lowest such value for the HF work, implying less exothermic solvation effects for the  $N_2$  system than for the HF systems. This is as expected in view of the exoenergetic contribution of ion-permanent dipole interactions which must occur in the latter systems. Also, the Henry's law constants observed in the HF work are about ten times greater than the values observed for the  $N_2$  system. This may again be partially attributable to such ion-dipole solvation effects occurring in the HF systems. In addition, the relatively high stability of NaF-HF complexes occurring in these systems no doubt serves to increase HF solubility and to make the heat of solution still more negative (15).

The  $\Delta S_p$  entropies of solution found in the HF work varied from -14.0 e.u., for the 45 mole % NaF system, to -15.2 e.u. for the 80.5 mole % NaF system (15). The value of -16.6 e.u. obtained for  $N_2$  in  $NaNO_3$  therefore appears reasonable in comparison to these values for other diatomic molecules. These entropies of solution for  $N_2$  and HF diatomic molecules are noticeably more negative than values obtained for monatomic noble gases in fluoride melt; (8, 9). This observation was predicted, since at higher temperatures a non-spherical gas molecule rotates more freely and the "surface area" of its cavity is correspondingly increased, leading to a more negative entropy of solution than for a spherically symmetric rare gas atom (8).

Copeland and Zybko have observed Henry's law constants for high pressure solubilities of Ar (18) and He (19) in molten  $NaNO_3$  at 642°K. For Ar:

$$K_{p,Ar} = (17.2 \pm 1.7) \times 10^{-7} \text{ mole cm.}^{-3} \text{atm.}^{-1}$$

and for He:

$$K_{p,He} = (22.7 \pm 0.7) \times 10^{-7} \text{ mole cm.}^{-3} \text{atm.}^{-1}.$$

The close-packed "spherical" radius of the  $N_2$  molecule is very nearly the same as that of Ar (1.92 Å)(9). Thus, the cavity creation work done against the comparatively small surface tension of  $NaNO_3$  by either gas would be expected to be small and approximately the same for both. However, the polarizability of  $N_2$  is  $1.734 \times 10^{-24} \text{ cm.}^3 \text{ molecule}^{-1}$ , as compared to  $1.626 \times 10^{-24} \text{ cm.}^3 \text{ molecule}^{-1}$  for Ar (26). On this basis, one would expect slightly greater ion-induced dipole solvation effects for  $N_2$  than for Ar, which would tend to make the former slightly more soluble if all other effects are nearly equal. This is demonstrated by the slightly greater solubility of  $N_2$  at 641.5°K. The polarizability of He is only about  $0.2036 \times 10^{-24} \text{ cm.}^3 \text{ molecule}^{-1}$  (26), and its close-packed radius is about 1.22 Å (9).

Thus, much less work against surface tension is required to create a hole for a He atom than for either  $N_2$  or Ar. However, solvation effects for He would be practically nonexistent. It would appear, therefore, that the slightly greater solubility of He may be primarily the result of the relative ease of introducing such a small atom into the liquid, in spite of the partially compensating solvation effects which exist for the larger solute molecules.

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LITERATURE CITED

1. A. E. Markam and K. A. Kobe, Chem. Rev., 28, 519 (1941).
2. J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," 3rd ed., Dover Publications, Inc., New York, N.Y., 1964, 488pp.
3. M. W. Cook, U. S. Atomic Energy Commission, UCRL-2459 (1954).
4. H. L. Clever, R. Battino, J. H. Sayler, and P. M. Gross, J. Phys. Chem., 61, 1078 (1957).
5. H. L. Clever, J. H. Sayler, and P. M. Gross, ibid., 62, 89 (1958).
6. L. W. Reeves and J. H. Hildebrand, J. Am. Chem. Soc., 79, 1313 (1957).
7. E. Nussbaum and J. B. Hursh, J. Phys. Chem., 62, 81 (1958).
8. W. R. Grimes, N. V. Smith, and G. M. Watson, ibid., 62, 862 (1958).
9. M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, ibid., 63, 1164 (1959).
10. R. B. Evans III, W. R. Grimes, N. V. Smith, and G. M. Watson, J. Chem. Eng. Data, 7, 285 (1962).
11. G. M. Barrow, "Physical Chemistry," McGraw Hill Book Co., Inc., New York, N.Y. 1961, pp. 481-483.
12. G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed., revised by K. S. Pitzer and L. Brewer, McGraw Hill Book Co., Inc., New York, N. Y., 1961, pp. 231-240.
13. H. H. Uhlig, J. Phys. Chem., 41, 1215 (1937).
14. F. H. Stillinger, Jr., in "Molten Salt Chemistry," M. Blander editor, Wiley-Interscience, New York, N. Y., 1964, pp. 87-105.
15. J. H. Shaffer, W. R. Grimes, and G. M. Watson, J. Phys. Chem., 63, 1999 (1959).
16. W. C. Zybko, "Effects of Inert Gas Pressure and Solubility on Electrical Conductance of Fused  $\text{NaNO}_3$ ," Ph.D. Thesis, Kansas State University, 1965, p. 15.
17. F. Din, "Thermodynamic Functions of Gases," vol. 3, Butterworth and Co., Ltd., London, 1961, pp. 146-150.
18. J. L. Copeland and W. C. Zybko, J. Phys. Chem., 69, 3631 (1965).
19. J. L. Copeland and W. C. Zybko, ibid., 70, 181 (1966).
20. B. B. Owens, private communications to J. L. Copeland, 1965.

21. H. Bloom, I. W. Knaggs, J. J. Molloy, and D. Welch, Trans. Faraday Soc., 49. 1458 (1953).
22. C. C. Addison and J. M. Goldrey, J. Chem. Soc., 1961, 468.
23. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 40th ed., 1959, p. 656.
24. W. J. Moore, "Physical Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 3rd ed., 1962, p. 229.
25. J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Dover Publications, New York, N. Y., 1946, pp. 563, 623.
26. E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, Oxford, 2nd ed., 1961, p. 383.

### VITA

The author was born in Winnsboro, South Carolina on January 22, 1941. At the age of five, he moved to Greensboro, North Carolina, where, after attending Mt. Zion Elementary School, he received his high school education at the James B. Dudley High School. He enrolled at the Agricultural and Technical College of North Carolina in the fall of 1959 and received the degree Bachelor of Science in June, 1963.

He entered the Graduate School of Kansas State University in September, 1963, and in June of 1966 he was awarded the degree of Master of Science by Kansas State University.

The author is a member of Beta Kappa Chi National Scientific Honor Society, Alpha Kappa Mu National Honor Society, and Alpha Chi Sigma National Chemical Fraternity.

### Publications

1. C. H. Edwards, L. Seibles, et.al., "Chromatography of the Methyl Esters of Selected Fatty Acids on Glass Fiber Paper," J. Chromatog. II, 349-354 (1963).
2. J. L. Copeland and L. Seibles, "The High-Pressure Solubility of Nitrogen in Fused Sodium Nitrate; Temperature and Pressure Dependences, and the Heat and Entropy of Solution," J. Phys. Chem., 70, (accepted) (1966).

SOLUBILITY OF NITROGEN  
IN FUSED SODIUM NITRATE

by

LAWRENCE SEIBLES

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AN ABSTRACT OF A THESIS

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The purpose of this work is to present new data on the solubility of gases in molten salt systems. A Parr Inconel metal bomb with chromel-alumel thermocouples was used to study the temperature and high-pressure dependences of the solubility of  $N_2$  in molten  $NaNO_3$ .

Eight solubility-pressure isotherms for  $N_2$  in fused  $NaNO_3$  were obtained, each consisting of four or five solubility-pressure points. The solubilities ranged from  $2.75 \times 10^{-4}$  moles  $cm^{-3}$ , at  $655.5^\circ K$  and 148 atm., to  $7.40 \times 10^{-4}$  moles  $cm^{-3}$  at  $686.5^\circ K$  and 426 atm. Average Henry's law constants,  $K_p$ , varied from  $(20.2 \pm 0.4) \times 10^{-7}$  mole  $cm^{-3}$  atm. $^{-1}$  at  $628.5^\circ K$  to  $(15.2 \pm 1.2) \times 10^{-7}$  mole  $cm^{-3}$  atm. $^{-1}$  at  $727.0^\circ K$ . Experimental values of  $\Delta H = -2.73 \pm 0.09$  kcal. mole $^{-1}$  and  $\Delta S_p = -16.6 \pm 0.1$  e.u. were obtained from the plot of  $\log K_p$  versus  $1/T$  and the theoretical thermodynamic relation.

The negative temperature coefficient of solubility for  $N_2$  in fused  $NaNO_3$ , and the attendant exothermic heat of solution are interpreted on the basis that the solvation effects in the system are of greater importance than the work required to create a cavity for a solute molecule. This interpretation is also supported by the fact that experimental distribution ratios,  $K_C$ , are larger than the theoretical values. The results also indicate that for molecules of nearly the same size, greater solubility in a given medium occurs for the more polarizable molecule.